John von Neumann Institute for Computing

Relativistic electronic-structure calculations for molecules

Markus Reiher and Bernd Heß

published in

Modern Methods and Algorithms of Quantum Chemistry,
J. Grotendorst (Ed.), John von Neumann Institute for Computing, Jülich, NIC Series, Vol. 1, ISBN 3-00-005618-1, pp. 451-477, 2000.

http://www.fz-juelich.de/nic-series/

RELATIVISTIC ELECTRONIC-STRUCTURE CALCULATIONS FOR ATOMS AND MOLECULES

MARKUS REIHER AND BERND A. HESS
Chair of Theoretical Chemistry
Friedrich–Alexander-Universität Erlangen–Nürnberg
Egerlandstr. 3
91058 Erlangen, Germany
E-mail: {Markus.Reiher, Hess}@chemie.uni-erlangen.de

We give an account of theoretical methods for calculations on atoms and molecules in a relativistic quantum-mechanical framework. After a short introduction into the nature of relativistic effects, we describe fully numerical methods for 4-component atomic structure calculations. The account closes with a detailed discussion of approximate relativistic methods for the description of the electronic structure of molecules.

1 Qualitative description of relativistic effects

At the beginning of the last century, Albert Einstein discovered the special and general theory of relativity which turned out to be the key to a unified description of classical mechanics and electrodynamics. It turns out that in particular in the case of fast-moving particles, non-relativistic mechanics is an approximation to relativistic physics. In the framework of non-relativistic quantum mechanics, methods have been developed to accurately describe the electronic structure of light atoms and molecules consisting of light atoms. Most organic compounds belong to this category, but even in these cases there are subtle effects requiring a relativistic treatment, which are important for the interpretation of highly accurate experiments in spectroscopy. The so-called relativistic effects begin to play a major role in heavy atoms and their compounds. This is due to the fact that the relativistic effects on energies and other physical quantities increase with the fourth power of the nuclear charge Z.

At the first glance, relativistic quantum chemical calculations are much more expensive than their non-relativistic analogues are. This is due to the fact that any relativistic theory has to consider for every particle also the degrees of freedom for its charge-conjugated particle (the positron in the case of the electrons of an atom or a molecule) on equal footing. Since there is an additional doubling of the degrees of freedom because the spin of the electron plays a dynamical role in relativistic theories and, therefore, also has to be treated explicitly, the Dirac equation, which is the proper equation of motion for spin one-half particles like electrons, consists essentially of four coupled differential equations.

The field dealing with relativistic electronic-structure theory of atoms and molecules is often called Relativistic Quantum Chemistry. It has been developing rapidly in the last few decades, and meanwhile very good reviews are available, which provide a much more detailled discussion of relativistic effects than we shall be able to give [1,2,3,4,5]. An excellent account on the literature dealing with relativistic quantum chemistry has been provided by Pyykkö and can be found in [6,7]

and also online in the WWW [8].

1.1 Direct relativistic effects

Relativistic effects in atoms and molecules may be divided into kinematical effects, which do not cause a splitting of energy levels due to the spin degrees of freedom, and into effects of spin–orbit coupling. Kinematical effects are caused by electrons moving with high velocity in the vicinity of a (heavy) nucleus. This leads to contracted orbitals and, thus, to a contracted electron density distribution in a quantum-mechanical description. Connected with this contraction is a lowering of orbital energies and of the total energy (if compared in the energy scale of the non-relativistic energies). This direct influence of relativistic kinematics is termed as *direct relativistic effects*. It is mainly important for s and $p_{1/2}$ shells, since these have appreciable amplitude in the vicinity of the nucleus. Obviously, these effects show up in physical quantities like excitation energies, ionization energies, and electron affinities, as well as in chemical quantities like electronegativity.

1.2 Indirect relativistic effects

Orbitals with higher angular momentum have a node at the nucleus and therefore are hardly directly affected by direct kinematical relativistic effects. The modified shielding of the nuclear charge by the contracted core orbitals results, however, in an expansion mainly of the d and f orbitals. These effects are called *indirect relativistic effects*.

2 Fundamentals of relativistic quantum chemistry

The time-dependent Schrödinger equation is not Lorentz invariant, which becomes immediately clear if one observes that all differential operators for spatial coordinates represent second derivatives while the time coordinate occurs as a first derivative. But spatial and time coordinates must be treated, roughly speaking, in an equivalent way by a physical theory.

In 1928, Dirac found an equation for the free motion of an electron which fulfills the invariance demands:

$$-i\frac{\partial\Psi(\mathbf{r},t)}{\partial t} = \hat{H}_D\Psi(\mathbf{r},t), \tag{1}$$

with the Dirac Hamiltonian

$$\hat{H}_D = c\boldsymbol{\alpha}\cdot\hat{\mathbf{p}} + m_0c^2\beta \quad , \tag{2}$$

and the standard definition for the momentum operator

$$\hat{\mathbf{p}} = -i\hbar\nabla \ , \tag{3}$$

where c is the speed of light, m_0 the rest mass of the electron and in the standard representation of the 4×4 matrices α and β, the latter a diagonal matrix

$$\beta = \begin{pmatrix} \mathbf{1}_2 & \mathbf{0} \\ \mathbf{0} & -\mathbf{1}_2 \end{pmatrix} \ , \tag{4}$$

with

$$\mathbf{1}_2 = \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix} \quad , \quad \mathbf{0} = \begin{pmatrix} 0 & 0 \\ 0 & 0 \end{pmatrix} \quad . \tag{5}$$

and the 3-component vector $\boldsymbol{\alpha}$= $(\boldsymbol{\alpha}_x, \boldsymbol{\alpha}_y, \boldsymbol{\alpha}_z)$ is conveniently expressed by means of Pauli's spin matrices σ_s as

$$\boldsymbol{\alpha}_s = \begin{pmatrix} \mathbf{0} & \sigma_s \\ \sigma_s & \mathbf{0} \end{pmatrix} \ , \ s = x, y, z \ , \tag{6}$$

with the Pauli matrices

$$\sigma_x = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} \ , \ \sigma_y = \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix} \ , \ \sigma_z = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} \quad . \tag{7}$$

Dirac's equation is essentially a set of four coupled differential equations, and the wavefunction appears to be a 4-component spinor containing four functions. Dirac found that four is the lowest dimension possible for an equation for a spin one-half particle consistent with the relativistic invariance requirement.

In the Dirac equation, the electromagnetic field is introduced by means of external potentials. This is very much akin to the method of introducing potentials into non-relativistic equations by the method of "minimal coupling". A fully relativistic theory requires, however, that the degrees of freedom are quantized as well, a procedure carried out in quantum electrodynamics, and leading to deviations from the Coulomb interactions, which is only the first term of a series in the fine-structure constant $\alpha = e^2/\hbar c$. Thus, for the case of many interacting electrons, the so-called Dirac-Coulomb operator, which features the Coulomb repulsion between the electrons in addition to a Dirac operator for each particle, does *not* satisfy the relativistic invariance requirements, i. e., invariance with respect to Lorentz transformations. Thus, relativistic electronic structure calculations with four-component wave functions and the Dirac-Coulomb operator are *not* "fully" relativistic, as often claimed, but rather correct only to first order in the fine-structure constant. The so-called Breit operator introduces the next higher order in the electron–electron interaction operator.

3 Numerical 4-component calculations for atoms

Before we discuss the methods for the calculation of electronic structure for *molecules* in greater detail, we shall make some comments on *atoms*. Obviously, the same theory which can be used for the treatment of molecules also applies for atoms. But there are some methods which can be used in particular for atoms because of their spherical symmetry.

4 A short history of relativistic atomic structure calculations

Some important landmarks in the history of relativistic atomic structure calculations will be given here. We refer to the literature [9,10,11] for detailed discussions on this subject.

Numerical relativistic calculations of atoms with more than one electron started in 1935: Bertha Swirles [12] transferred the Hartree-Fock formalism to the Dirac equation. Due to the lack of computers at that time, only a few calculations could be carried out. The situation changed in the 1960's when Grant used the tensor algebra introduced by Racah (cf., e. g., [13,14]) for handling the analytic integration over all angular dependent terms and derived a general expression for the total electronic energy of a closed-shell atom in the central-field approximation. From this expression he deduced self-consistent field (SCF) equations for the determination of spinors [15,16,17].

In 1967, Kim [18] expressed the SCF equations within a basis set representation of the spinors. Desclaux [19] calculated highly accurate (fully numerical) spinor energies, total energies, and other expectation values for nearly all neutral atoms of the periodic table in the Dirac-Fock (DF) approximation, i. e., for closed shells and configuration averages. He also published a program for calculations on the multi-configuration (MC)DF level in 1975 [20]. In 1980 Grant *et al.* published their MCDF code [21,22] which was later reorganized into the GRASP package [23]. The numerical methods they used [24] are similar to those applied in Desclaux's code [25]. But there were (and still are) SCF convergence problems in some cases. Parpia *et al.* extended the code to facilitate large-scale computations through the use of dynamic memory allocation and improved convergence features (GRASP92 [26]). Additionally, there has been done work on relativistic basis set calculations for atoms during the last two decades (see for example [27,28,29]). Recently developed program packages for relativistic 4-component molecular electronic structure calculations can also be used for the calculation of the electronic structure of atoms (cf., e. g., [30,31,32,33,34,35]).

4.1 Reduction to equations dependent on the radial coordinate

When we assume that the mass of the atom's nucleus is infinitely large (as compared to the electron's mass) we describe the motion of the electrons in a central field potential. The spherical symmetry of this central field potential allows us to use the following ansatz for the 4-component spinor

$$\psi_p(\mathbf{r},\sigma) = \frac{1}{r}\begin{pmatrix} P_{n_p\kappa_p}(r)\;\Omega_{\kappa_p m_p}(\vartheta,\varphi,\sigma) \\ \mathrm{i}Q_{n_p\kappa_p}(r)\;\Omega_{-\kappa_p m_p}(\vartheta,\varphi,\sigma) \end{pmatrix}\;, \tag{8}$$

where $\Omega_{\kappa_p m_p}(\vartheta,\varphi,\sigma)$ are 2-component spherical spinors containing the vector coupling of angular momentum and spin (κ_i is the relativistic angular momentum quantum number). With this ansatz it is possible to treat all angular and spin dependent parts analytically. What remains is the calculation of the two radial functions $P_{n_p\kappa_p}(r)$ and $Q_{n_p\kappa_p}(r)$. Note that for this task coupled first-order differential equations have to be solved, e. g., the Dirac-Fock equations [17,36]

$$\begin{pmatrix} V_i^P(r)-\epsilon_i & A_i^\dagger(r) \\ A_i(r) & V_i^Q(r)-\epsilon_i \end{pmatrix}\begin{pmatrix} P_i(r) \\ Q_i(r) \end{pmatrix} = \begin{pmatrix} X_i^P(r) \\ X_i^Q(r) \end{pmatrix}\;, \tag{9}$$

in case of closed-shell atoms. Here we introduced the following functions

$$A_i(r) = c\left(\frac{\mathrm{d}}{\mathrm{d}r} + \frac{\kappa_i}{r}\right) \ , \tag{10}$$

$$V_i^Q(r) = V_i^P(r) - 2c^2 \ , \tag{11}$$

$$V_i^P(r) = V_{\mathrm{nuc}}(r) + \sum_j D_j U_{jj0}^C(r) - \sum_{\nu=0}(D_i/2)\,\Gamma_{ii\nu} U_{ii\nu}^C(r) \ , \tag{12}$$

$$X_i^R(r) = \sum_{j,j\neq i}\sum_{\nu}(D_j/2)\,\Gamma_{ij\nu} U_{ij\nu}^C(r) R_j(r) \ , \tag{13}$$

$$R_j(r) = P_j(r) \text{ or } R_j(r) = Q_j(r)$$

$$\Gamma_{ij\nu} = 2\begin{pmatrix} j_i & \nu & j_j \\ 1/2 & 0 & -1/2 \end{pmatrix}^2 \ . \tag{14}$$

The $\Gamma_{ij\nu}$ are the reduced two-electron Coulomb structure factors (coupling coefficients) originating from the analytical treatment of spin and angular momentum. The potential functions $U_{ij\nu}^C(r)$ are defined as

$$U_{kl\nu}^C(r_1) = \int_0^\infty [P_k(r_2)P_l(r_2) + Q_k(r_2)Q_l(r_2)]\frac{r_<^\nu}{r_>^{\nu+1}}\,dr \ , \tag{15}$$

where $r_{<,>}$ is the minimum and maximum, resp., of $\{r_1, r_2\}$. $D_i = 2|\kappa_i|$ denotes the occupation number of the i-th shell. The sums over ν result from the analytic treatment of angular and spin parts and run from $\nu_{\min} = |j_i - j_j|$ to $\nu_{\max} = j_i + j_j$ (constraints: $j_i + j_j + \nu$ has to be even if $\mathrm{sgn}(\kappa_i) \neq \mathrm{sgn}(\kappa_j)$ and $j_i + j_j + \nu$ has to be odd if $\mathrm{sgn}(\kappa_i) = \mathrm{sgn}(\kappa_j)$).

These SCF equations contain the r variable only and are, thus, one-dimensional. This makes them accessible for numerical solution methods which work particularly well for one-dimensional equations.

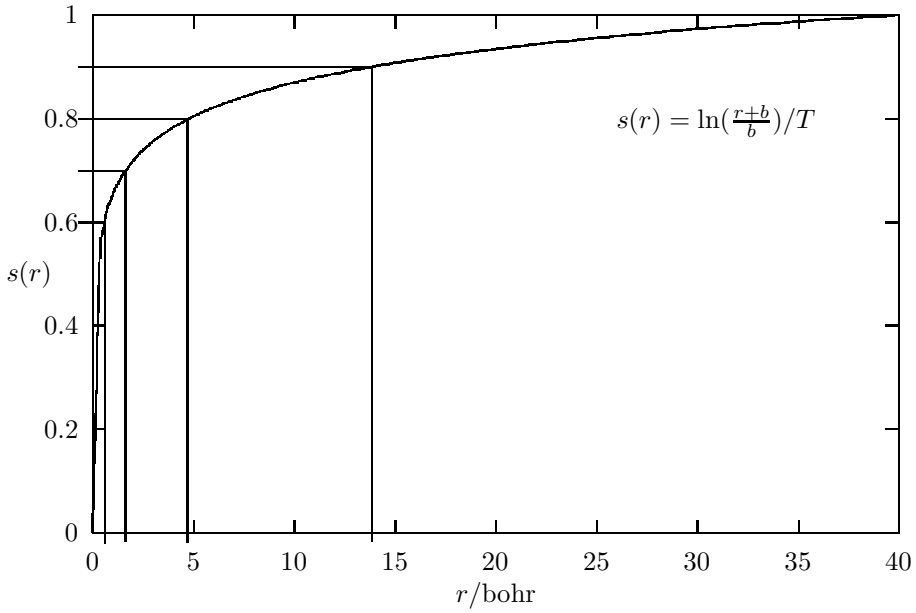
4.2 Numerical solution techniques

In atomic structure theory highly accurate calculations are possible. This high accuracy is guaranteed by the employment of fully numerical solution techniques which do not make use of basis sets such that a discussion of the size of a basis set is not necessary. Furthermore, the use of basis sets is more involved in relativistic electronic structure calculations as compared to non-relativistic analogues which we will see later on.

Finite-difference methods operating on a grid consisting of equidistant points ($\{x_i\}, x_i = ih + x_0$) are known to be the most accurate techniques available. Additionally, on an equidistant grid all discretized operators appear in a simple form. The uniform step size h allows us to use the Richardson extrapolation method [37,38] for the control of the numerical truncation error. Many methods are available for the discretization of differential equations on equidistant grids and for the integration (quadrature) of functions needed for the calculation of expectation values.

Since a discretization in the variable r is not efficient (too many grid points would lie at large distances instead near the origin where they are needed), a variable transformation is introduced. In this new variable s the equidistant grid is

Figure 1. An example for a variable transformation function $r \mapsto s = s(r)$ of typical shape (logarithmic grid: b=0.001, $T = \ln[(r_{max} + b)/b]$, and r_{max}=40). The horizontal lines indicate the equidistant s-grid while the vertical lines demonstrate how the r-grid is then generated.



created and all differential equations to be solved have to be transformed to this new variable s. Fig. 1 shows how such a transformation function must principally look like.

Simple discretization schemes use derivatives of Lagrangian interpolation polynomials that approximate the function known only at the grid points $\{x_i\}$. These schemes consist of tabulated numbers multiplied with the function's values at m contiguous grid points and are referred to as "m-point-formulae" by Bickley [39] (cf. [p. 914][40]). For an acceptable truncation error $O(h^t)$, $t = 4$ or higher, m is larger than t which leads to an extended amount of computation. Efficient discretization schemes are available for the discretization of the differential equation encountered in the course of a quantum chemical electronic structure calculation (cf., e. g., [41,42,43,44].

Once a discretization scheme is chosen numerical solution methods like inverse iteration, shooting methods etc. can be applied to solve the problem and obtain values for the radial functions at equidistant grid points. These are implemented in standard computer programs [23,26,45].

4.3 Description of the positive charge of the nucleus

The choice of a point-like atomic nucleus (PNC) limits the calculations to atoms with a nuclear charge number $Z \leq c$, i. e., $Z_{max} \approx 137$. The series expansion around the origin for a non-singular electron-nucleus potential shows (see below) that this

limit can be overcome using an atomic nucleus of finite size with a model function for the description of the distribution of the positive charge inside the nucleus (we will denote this choice as FNC for *finite nucleus case*). The FNC limit for the nuclear charge number Z is approximately 170 due to the one-particle energies of the electrons entering the negative continuum.

Theoretical nuclear physics does not provide a unique model function for the positive charge distribution derived from quantum chromodynamics. That is why there is a certain degree of arbitrariness in the choice of such functions.

The potential corresponding to a given model charge density distribution $\rho(u)$ is

$$-rV(r) = 4\pi \int_0^r \rho(u)u^2 du + 4\pi r \int_r^\infty \rho(u)u du \ . \tag{16}$$

Many model potentials $V(r)$ have been used but three became important in electronic structure calculations:

4.3.1 A piecewise defined model: Homogeneous charge density distribution

The uniformly or homogeneously charged sphere is a simple model for the finite size of the nucleus. The total nuclear charge $+Z$ is uniformly distributed over the nuclear volume $4/3\pi R^3$,

$$\rho_{\rm hom}(r) = \begin{cases} 3Z/(4\pi R^3) & ; r \le R \\ 0 & ; r > R \end{cases} \ , \tag{17}$$

where R denotes an empirically fixed sphere radius (the "size" of the nucleus). This charge density distribution leads to the homogeneous electron-nucleus potential

$$V_{\rm hom}(r) = \begin{cases} -\frac{Z}{2R}\left[3 - \frac{r^2}{R^2}\right] & ; r \le R \\ -Z/r & ; r > R \end{cases} \ , \tag{18}$$

provided that the charge density distribution is normalized to the total charge

$$4\pi \int_0^\infty \rho_{hom}(u)u^2 du = Z \ . \tag{19}$$

4.3.2 Continuously defined models: Gaussian and Fermi charge density distributions

The Gaussian charge density distribution

$$\rho_{\rm gauss}(r) = \rho_{\rm gauss,0} \exp\left[-r^2/R^2\right] \tag{20}$$

with $\rho_{\rm gauss,0}$ fixed through the normalization condition,

$$\rho_{\rm gauss,0} = \frac{Z}{4\pi} \frac{1}{\sqrt{\pi}R^3} \ , \tag{21}$$

leads to the following electron-nucleus potential

$$V_{\rm gauss}(r) = -\frac{Z}{r}{\rm erf}[r/R] \tag{22}$$

(erf[x] is the error function). The Fermi distribution,

$$\rho_{\rm fermi}(r) = \rho_{\rm fermi,0} f \left[1 + \exp\left[(r-R)/(cR)\right]\right]^{-1} \ , \tag{23}$$

is another nuclear charge model often used in atomic structure calculations although the evaluation of the corresponding potential is quite difficult.

4.4 Drawbacks of the choice for the nuclear charge distribution

We suppose the radial functions to be analytic at the origin (the shell index i of the expansion coefficients $a_j^{(r)} = a_{j,i}^{(r)}$ and $b_j^{(r)} = b_{j,i}^{(r)}$ is skipped for the sake of brevity),

$$P_i(r) = r^{\alpha_i} \sum_{j=0}^{\infty} a_j^{(r)} r^j \ , \tag{24}$$

$$Q_i(r) = r^{\alpha_i} \sum_{j=0}^{\infty} b_j^{(r)} r^j \ , \tag{25}$$

and determine the first exponent of this series expansion α_i by solving the SCF equation for the ith shell using series expansions for the coefficient functions[a]:

$$V_i^P(r) = v_{-1}^{(r)} r^{-1} + v_0^{(r)} + O(r^k) \ , \tag{26}$$

$$X_i^{P,Q}(r) = x_{-1}^{(r)} r^{-1} + x_0^{(r)} + O(r^k) \ , \tag{27}$$

with

$$v_{-1}^{(r)} = \begin{cases} -Z \text{ in the PNC} \\ \ \ 0 \text{ in the FNCs} \end{cases} \ . \tag{28}$$

Here we assume (which might not be true in the general MCDF case) that the inhomogeneity vanishes at the origin, i. e., $x_{-1}^{(r)} = x_0^{(r)} = 0$. We obtain from the SCF equations for the coefficients of the $r^{\alpha_i - 1}$ term

$$(v_{-1}^{(r)}/c)\, a_0^{(r)} + (\kappa_i - \alpha_i) b_0^{(r)} = 0 \ , \tag{29}$$

$$(v_{-1}^{(r)}/c)\, b_0^{(r)} + (\kappa_i + \alpha_i) a_0^{(r)} = 0 \ , \tag{30}$$

which yields

$$\alpha_i = \sqrt{\kappa_i^2 - (v_{-1}^{(r)})^2/c^2} = \begin{cases} \sqrt{\kappa_i^2 - Z^2/c^2} & , \text{ PNC} \\ |\kappa_i| & , \text{ FNCs} \end{cases} \ . \tag{31}$$

For PNC the first exponent of the series expansion is **not** integral. This creates substantial drawbacks for the numerical methods used, which always require finite higher derivatives which become singular at the origin.

[a] The potential functions $U_{kl\nu}(r)$ can contribute only to the r^j terms (with $j \geq 0$).

4.5 Technical problems in relativistic electronic structure calculations for atoms

In general, technical problems usually remain in the group working on the implementation of some theory into a computer program. Since this winterschool is mainly devoted to the discussion of problems, which one gets involved into when implementing a formalism, some peculiarities are discussed in the following sections.

4.5.1 Transformation to orbitals which are regular at the origin

As was pointed out in the previous section, a singular electron-nucleus potential of Coulomb type yields non-analytic solution functions. To obtain regular functions for the PNC the operator identity

$$\frac{d}{dx} = x^{-\gamma_i} \frac{d}{dx} x^{\gamma_i} - \frac{\gamma_i}{x} \tag{32}$$

with

$$\gamma_i = |\kappa_i| - \alpha_i = |\kappa_i| - \sqrt{\kappa_i^2 - (Z/c)^2} \tag{33}$$

suggested by Biegler-König [46] can be used to replace the differential operator d/dr in the SCF equations. The power γ_i depends on the quantum number κ_i and is chosen such that it cancels out the real power α_i in the short-range series expansion and replaces it by the integral number $|\kappa_i|$. A generalized distance variable x is chosen in Eq. (32) to indicate that the identity may be introduced in the old variable r or in the new variable s.

4.5.2 Extrapolation techniques for efficient algorithms

Finite difference methods allow the use of techniques which extrapolate to step size $h \to 0$ (i. e., the exact solution) and control the numerical truncation error [38,47,48]. This can be done for every numerically calculated quantity F if we assume an analytic behaviour of F,

$$F(h) = F(0) + Ah^t + O(h^{t+1}) \ , \tag{34}$$

where t is the order of the truncation error connected to the chosen numerical method. If F is known for three different step sizes the quantities $F(0)$ (the extrapolated result for step size zero), A, and t can be calculated. Since all numerical methods are usually employed with an order $t \geq 4$, this can be used to check this "theoretical order". Note that the extrapolated value $F(0)$ will be correct to order $t + 1$ and we gain only one or two figures in accuracy compared to the result calculated with the largest number of grid points.

Multigrid methods with control of the numerical truncation error are very useful for the solution of matrix equations since they start with a small number of grid points, use extrapolation techniques similar to Richardson's and reduce the step size until the result is accurate enough. The method of Bulirsch and Stoer (cf. [p. 718-725][47] and [p. 288-324][49]), for instance, consists essentially of three ideas:

- The calculated values for a given step size h are analytic functions of h — which is, of course, fulfilled here.
- The analytic expression can always be approximated as a rational function,i. e., a quotient of two polynomials in h, which is the basis for the rational extrapolation [p. 104-107] [47].
- The applied numerical method must be of even order in all higher corrections in the truncation term in order to gain two orders at a time [p. 717][47].

The SCF equations are now solved for a given number of points. Then, mid-points are added to this starting grid and the equations are solved again. This process is repeated until the rational extrapolation leads to a sufficiently small degree of error. A 3-point formula [p. 914][40] without origin correction for the first derivative, which is only of second order in h, can be applied for the discretization. This is possible since the numerical error is controlled by rational extrapolation. Its advantage is that the discretization matrix in the equation to be solved in the SCF procedure is only penta-diagonal and its elements are easily computed. Additionally, the Bulirsch-Stoer method might also be used in cases where one would like to use a diagonal representation for the coefficient functions of the differential equations for reasons of numerical stability.

4.5.3 Corrections for the electron-electron interaction: Breit interaction

As mentioned above, the electron–electron interaction is known from QED only as a series expansion, which in addition depends on the gauge fixing employed for the electromagnetic field. The first relativistic correction to the two-electron Coulomb operator is the Breit operator,

$$B_\omega(1,2) = -\frac{\boldsymbol{\alpha}_1\boldsymbol{\alpha}_2\cos(\omega r_{12})}{r_{12}} + (\boldsymbol{\alpha}_1\nabla_1)(\boldsymbol{\alpha}_2\nabla_2)\frac{\cos(\omega r_{12})-1}{\omega^2 r_{12}} \ , \tag{35}$$

where $\boldsymbol{\alpha}_i$ are the standard Dirac matrices with respect to electron i. The electron-electron distance vector is denoted as $\mathbf{r}_{12}$ and its length is r_{12}. The frequency of the exchanged photon divided by the speed of light c is ω. The Breit operator may be written in its long wavelength limit as

$$B_0(1,2) = -\frac{\boldsymbol{\alpha}_1\boldsymbol{\alpha}_2}{r_{12}} - \frac{1}{2}(\boldsymbol{\alpha}_1\nabla_1)(\boldsymbol{\alpha}_2\nabla_2)r_{12} + O(\omega^2 r_{12}) \ , \tag{36}$$

where we used the Taylor series expansion for the cosine. This expression is equivalent to the original one given by Breit [50,51,52]

$$B_0(1,2) = -\frac{\boldsymbol{\alpha}_1\boldsymbol{\alpha}_2}{r_{12}} + \frac{1}{2r_{12}}\left(\boldsymbol{\alpha}_1\boldsymbol{\alpha}_2 - \frac{(\boldsymbol{\alpha}_1\mathbf{r}_{12})(\boldsymbol{\alpha}_2\mathbf{r}_{12})}{r_{12}^2}\right). \tag{37}$$

The Breit interaction becomes important for the calculation of fine structure splittings and for highly charged ions. Unfortunately, it turns out that the calculation of the matrix elements resulting from this operator may become cumbersome and time consuming even in the frequency-independent limit, $\omega \to 0$.

For historical reasons, the Breit operator was split into the Gaunt term (first term in the operator given in Eq. (37)) and the retardation term. While the Gaunt

term leads to matrix elements which are comparable in complexity to those obtained for the Coulomb interaction, the retardation term turns out to be more difficult to compute [17].

In 1976, Grant and Pyper [53] gave a general formulation of the **total** Breit interaction. Unfortunately, the individual matrix elements for the frequency-independent Breit interaction turned out to be non-symmetric in the electronic radial coordinates, r_1 and r_2, while the operator in its original form is symmetric in the total electronic coordinates. Their expression for the two-electron matrix element involves integrals over the radial variable r_2 which have to be evaluated for every value of r_1 which can become very time consuming (however, there exist some tricks which reduce the effort).

The fully numerical MCDF package GRASP includes the Breit interaction only as a first-order perturbation correction (after the self-consistent field (SCF) iterations converged with the Coulomb interaction terms only). Only the Gaunt interaction has been routinely treated in numerical calculations in a self-consistent way thus far. Note that the basis set approach is not affected by these problems.

For a long time it has been thought that the Breit interaction must not be evaluated self-consistently and should be treated only as a first-order perturbation. DF calculations have shown that the self-consistent calculation of the Breit interaction does not lead to instabilities. Since in numerical DF and in MCDF calculations the negative continuum is excluded, the treatment of the Breit interaction self-consistently leads to results comparable to those from all order perturbation theory.

A reformulation of the frequency-independent Breit operator yielding relatively simple expressions for the matrix elements and an algorithm which uses the same routines as in Coulomb-only calculations has been derived [54]. Table 1 shows some results obtained with this algorithm for the light atoms helium and beryllium. Two points are important in this context. First, the Breit contribution to the total energy is very small and roughly speaking of the order of effects coming from choosing different electron-nucleus potential or different values for the speed of light (the actual recommended value is $c = 137.0359895$, however, even in the recent literature the old value $c = 137.037$ is still in use). The small effect of the Breit correction implies that its fully numerical calculation is far from being trivial since very small numbers occur in iterative calculations.

4.5.4 Other relativistic corrections

The frequency-independent Breit interaction is by far not the only correction arising from quantum electrodynamics. Other corrections, like *self energy* or *vacuum polarization*, become also important. An exact calculation of electronic structure on a quantum electrodynamical basis is only possible for atoms with, say, one to three electrons (for a recent review see [56]).

The main problem for atomic structure calculations is that these correction terms cannot be easily included into the implemented framework since they cannot be reduced to simple radial-dependent potential functions (apart from the vacuum polarization for which the Uehling potential might be used).

Table 1. Relativistic and non-relativistic Dirac-Fock calculations on helium and beryllium. The results have been obtained with the fully numerical atomic structure program ADRIEN [55] (meaning of styles: *italics: relativistic effect*, **bold face: Breit effect**, `Typewriter: SCF effect`).

	type	this work[1]	ref. data	from
He	non-rel.		2.861679996	A
	DF-Coulomb	2.861*8133420*	2.861*813323*	B, GRASP
	Breit/pert.	2.861**7495464**	2.861**7495**	C, GRASP
	Breit/SCF	2.861**7495**455	2.861**749**0	D, basis-sets
Be	non-rel.		14.573023169	A
	DF-Coulomb	14.57*58917109*	14.57*5891698*	B, GRASP
	Breit/pert.	14.575**1892247**	14.575**1895**	C, GRASP
	Breit/SCF	14.575**1892**612	14.575**1891**	D, basis-sets

A Stiehler and Hinze, *unpublished* (1995) (numerical, point nucleus)

B Dyall and Visscher, *At. Data Nucl. Data Tables* (1997) **67**, 207 (numerical, "homogeneous" nucleus), and *http://theochem.chem.rug.nl/∼luuk/FiniteNuclei/*

C Parpia *et al.*, *J. Phys. B* (1992) **25**, 1 (numerical, "homogeneous" nucleus)

D Ishikawa *et al.*, *PRA* (1991) **43**, 3270 (basis sets, "homogeneous" nucleus, $c = 137.0370$)

[1] all calculations with 1000 grid points, "homogeneous" nucleus

4.5.5 Large CI calculations and generation of configuration state functions

While large configuration interaction (CI) calculations have become possible with the invention of the Davidson algorithm in the seventies of the last century [57,58], it has been adopted for relativistic atomic structure calculations twenty years later when Froese Fischer *et al.* introduced it into the GRASP package by Grant *et al.* [26] (for an application see, e. g., [59]).

Davidson's algorithm is designed for the calculation of a few eigenvectors of a large CI matrix by an iterative procedure. To set up this large $N \times N$ CI matrix it is necessary to construct the N-dimensional space spanned by the configuration state functions (CSFs) in jj coupling. This automatical construction of jj coupled CSFs is not trivial and routinely done in the framework of Racah algebra.

4.6 Outlook

Although atomic structure calculations have a very long history some techniques known in molecular quantum chemistry for a long time have never been implemented into existing fully numerical atomic structure programs. This is astonishing since these techniques are very promising. For example, the DIIS method by Pulay [60,61,62] could cure many of the SCF convergence problems known in relativistic atomic structure calculations.

Another example is the recently developed Jacobi-Davidson method by van der

Vorst *et al.* [63,64,65,66,67] which improves on the existing Davidson method for the determination of eigenvectors particular in CI problems.

5 Molecular Calculations

Whereas calculations on atoms are generally feasible with grid-based techniques, calculations on molecules commonly make use of expansion techniques. Very similar to non-relativistic wave functions, it is customary to expand molecular spinors in a basis of Gaussian functions. The most rigorous method for treating relativity in quantum chemical calculations then starts from the 4-component no-pair Dirac–Coulomb–Breit (DCB) Hamiltonian [68,69]. This Hamiltonian includes terms to second order in the fine-structure constant α, and is expected to be sufficiently accurate for neutral and weakly ionized states of even the heaviest atoms and molecules [70]. Calculations based on the DCB Hamiltonian may serve as reference for more approximate treatments of relativistic effects, such as perturbation theory, relativistic pseudo-potential techniques, and relativistic local density methods.

Four-component spinors obtained by solving single- or multiconfigurational Dirac–Fock equations provide a natural starting point for calculation of dynamic electron correlation effects, which are important in the quantitative determination of ground and excited states properties such as transition energies, electric and magnetic moments, or oscillator strengths. The coupled-cluster method has emerged as the most powerful tool for handling correlation effects in atomic and molecular systems (see [71] for a recent review). It includes correlation effects to high order and is size extensive, a property of particular importance for heavy systems, where relativistic effects are also most pronounced. Significant progress has been made recently in the development and application of the relativistic coupled-cluster method (RCC) to atoms. Some of these applications were done numerically [72,73] and others used basis sets, either local [74,75,76,77,78] or global [79,80,81,82,83,84].

Uzi Kaldor's group in Tel Aviv has recently developed and implemented a relativistic version of the multireference valence-universal Fock-space coupled-cluster method for atomic systems, using a discrete basis of four-component Gaussians spinors (G-spinors). The method starts from the DCB Hamiltonian and treats correlation by the coupled-cluster singles-and-doubles (CCSD) approximation, which includes single and double virtual excitations in a self-consistent manner, incorporating the effects of the Coulomb and Breit interactions to all orders in these excitations. Accurate ionization potentials, excitation energies and fine-structure splittings were obtained by this method for a variety of heavy and superheavy atomic systems [84,85,86,87,88,89,90,91,92]

Four-component correlation methods for molecules have become available only recently. They include relativistic configuration interaction (CI) [93], second order many-body perturbation theory (MBPT) [94], and relativistic coupled cluster (RCC) [95,96,97,98]. Both MBPT and RCC were used in a single-configuration version, suitable for limited classes of molecular states, with no degeneracy or near-degeneracy. The development and implementation of accurate relativistic 4-component multireference molecular approaches is a challenging problem. We are aware of only one such method based on the relativistic 4-component multiconfigurational SCF

approach [99]. Also by Kaldor's group, molecular single-reference four-component RCC code [98] has been developed.

Four-component methods usually involve complex spinors and place heavy demands on computational resources.

5.1 Two-Component Methods

While theoretically most appealing, the four-component methods are very expensive as concerns computational resources. This is, of course, because the charge-conjugated degrees of freedom are treated as dynamical variables and thus require their own basis set in the calculation. For technical reasons, the basis set for the small component tends to be even larger than the large component basis.

Since the charge-conjugated degrees of freedom are not excited at energies typical for the valence shell of neutral or mildly ionized atoms and molecules, it is desirable to integrate them out at the very beginning. This leads to a transformed Hamiltonian, operating on a two-component wave function for the electronic degree of freedom. Moreover, it is possible also for the Dirac equation to separate off spin-dependent terms rigorously [100], so that in many cases one can use a spin-averaged one-component wave function, calculated from a Hamiltonian transformed from the spin-free ("scalar relativistic") part of the Dirac equation. The transformed Hamiltonians are obtained by means of a unitary transformation that annihilates the coupling between the "electron-like" and the "positron-like" degrees of freedom. Their wave functions still have formally four components. Since, however, there is no coupling any more between the states of positive energy (the electrons) and the states of negative energy (the positrons), we now have the possibility to focus on the former and work with two-component wave functions only. While spin–orbit coupling is described in the "Dirac-like" (fourc component) representation by a purely algebraic structure (the Clifford algebra of the Dirac matrices), there is a "space part" of the spin–orbit coupling operator in the decoupled representation.

The decoupled representation is achieved by a unitary transformation

$$H^{\text{decoupled}} = U^\dagger D U = \begin{pmatrix} h_+ & 0 \\ 0 & h_- \end{pmatrix} \tag{38}$$

with

$$\begin{aligned} UU^\dagger &= 1 \\ U &= \begin{pmatrix} (1+X^\dagger X)^{-1/2} & (1+X^\dagger X)^{-1/2} X^\dagger \\ X(1+XX^\dagger)^{-1/2} & (1+XX^\dagger)^{-1/2} \end{pmatrix} \end{aligned} \tag{39}$$

and D denoting a Dirac-type Hamiltonian. The operator X maintains the exact relationship between the large and the small components

$$\phi_S = X\phi_L \tag{40}$$

for any trial function for the small component ϕ_S and for the large component ϕ_L. The operator X is not known in general. If (ϕ_S, ϕ_L) is an exact eigenfunction (ψ_L, ψ_S) of the one-electron Dirac equation, it could in principle be determined by

expressing the small component in terms of the large component by means of the coupled system of equations resulting from

$$\begin{aligned} c\boldsymbol{\sigma p}\,\psi_S + V\,\psi_L &= E\,\psi_L \\ c\boldsymbol{\sigma p}\,\psi_L - 2mc^2\,\psi_S + V\,\psi_S &= E\,\psi_S, \end{aligned} \tag{41}$$

using the expression for ψ_S from the lower equation

$$2mc^2\,\psi_S = \left(1 + \frac{E-V}{2mc^2}\right)^{-1} c\boldsymbol{\sigma p}\,\psi_L. \tag{42}$$

In the general case, X must fulfill the non-linear equation [101,102,103]

$$X = \frac{1}{2mc^2}\left(c\boldsymbol{\sigma p} - [X,V] - X(c\boldsymbol{\sigma p})X\right). \tag{43}$$

Obviously, the solution of this equation for X is as complex as the solution of the Dirac equation itself, and approximations have to be employed.

Since the transformed large component, now describing electron states only, should be normalized to one, the equation contains renormalization terms $(1 + X^\dagger X)^{-1/2}$ to take the change from the Dirac normalization prescription for any four-component wave function Φ

$$\begin{aligned} \langle\Phi|\Phi\rangle &= \langle\phi_L|\phi_L\rangle + \langle\phi_S|\phi_S\rangle \\ &= \langle\phi_L|\phi_L\rangle + \langle X\phi_L|X\phi_L\rangle \end{aligned} \tag{44}$$

into account. Unfortunately, closed-form solutions for Eq. (40) are known only for a restricted class of potentials [104]. A very important special case is, however, the free particle, defined by $V \equiv 0$. In this case, we find a closed-form solution

$$X^{V=0} = \left(mc^2 + \sqrt{m^2c^4 + p^2c^2}\right)^{-1} c\boldsymbol{\sigma p}. \tag{45}$$

This defines the *exact* Foldy-Wouthuysen transformation for the free particle. Note that the square root is not expanded here.

Early attempts to reduce the Dirac and Dirac–Coulomb–Breit Hamiltonian to the electronic degrees of freedom are characterized by expansions of the operators in powers of $(E-V)/mc^2$, the most popular of these methods being the Foldy–Wouthuysen transformation [105]. It has, however, been recognized early on that the resulting expressions are too singular beyond the first order of perturbation theory [106] and that, in particular, they cannot be used in a variational calculation. Variationally stable transformed Hamiltonians have appeared only recently in the literature [107,108,101]. Before introducing these methods in more detail, we shall briefly discuss the classical methods of reducing the Dirac equation to two components.

5.1.1 Elimination of the small component

The method of elimination starts from the Dirac equation in the split form Eq. (41). The expression for the small component obtained from the second of those equations is inserted into the first one, yielding

$$(V-E)\,\psi^L + \frac{1}{2mc^2}\left[\boldsymbol{\sigma p}\,\omega(\boldsymbol{r})\,\boldsymbol{\sigma p}\right]\psi_L = 0 \tag{46}$$

with

$$\omega(\boldsymbol{r}) = \left(1 - \frac{V-E}{2mc^2}\right)^{-1}. \tag{47}$$

This substitution leads to an equation for the large component only, and Eq. (47) has been used as the basis to formulate energy-dependent, non-hermitean operators [109,110,111,112,113,114,115,116]. If desired, the spin dependence can be isolated using

$$(\boldsymbol{\sigma u})(\boldsymbol{\sigma v}) = \boldsymbol{uv} + i\boldsymbol{\sigma}(\boldsymbol{u} \times \boldsymbol{v}). \tag{48}$$

The energy dependence is, however, undesirable, since orbital-dependent Hamiltonians and non-orthogonal orbitals result. The simplest way to arrive at a hermitean, energy-dependent operator is by expanding

$$\left(1 - \frac{V-E}{2mc^2}\right)^{-1} = \sum_{n=0}^{\infty} \left(\frac{V-E}{2mc^2}\right)^n. \tag{49}$$

Keeping only the lowest-order term, the non-relativistic Schrödinger equation is recovered. Low-order relativistic corrections can be extracted by keeping the next higher term and eliminating the energy dependence by means of systematic expansion in c^{-2}. This leads to the Pauli Hamiltonian

$$H_{\text{Pauli}} = \frac{p^2}{2m} + V + \frac{1}{4m^2c^2}\left(\frac{-p^4}{2m} + \frac{1}{2}(\Delta V) + \boldsymbol{\sigma}(\boldsymbol{\nabla} V) \times \boldsymbol{p}\right), \tag{50}$$

where the so-called mass–velocity term $-p^4/8m^3c^2$, the Darwin term $\Delta V/4m^2c^2$, and the spin–orbit coupling term $\boldsymbol{\sigma}(\boldsymbol{\nabla} V) \times \boldsymbol{p}/4m^2c^2$ describe relativistic corrections to $O(c^{-2})$. Several problems are connected with this operator: The minus sign of the mass–velocity term yields a strongly attractive term for states with high momentum, and leads to variational collapse in unconstrained variation; the Darwin term degenerates to a highly singular Delta-Function term in the case of the potential of a point-like nucleus; the spin–orbit coupling term leads to variational collapse as well, since it is not bounded below. These problems cannot be remedied by going to higher orders [106]. In fact, the expansion in Eq. (49) is invalid for $V - E > 2mc^2$, and this condition occurs certainly in regions close to the nucleus. Operators based on simple expansions of Eq. (49) in c^{-2} are in general singular and cannot be used for variational calculations. The Pauli operator is therefore defined only for perturbation theory to lowest order. In practical calculations, its expectation values give satisfactory relativistic corrections to the energy up to the first and second transition metal row.

Making use of special features of the matrix representation of the Dirac equation, Dyall has recently worked out a Modified Elimination of the Small Component [117,118]. His method takes the proper renormalization mentioned above into account. In particular this normalized variant of the Modified Elimination of the Small Component is free from the singularities which plague the classical elimination method. A very well-studied technique to arrive at regular expansions has been developed in the mid-eighties [101,102]. It is based on rewriting $\omega(\boldsymbol{r})$ in (47) and choosing a

different expansion parameter. Writing $\omega(\boldsymbol{r})$ as

$$\omega(\boldsymbol{r}) = \frac{2mc^2}{2mc^2 - V}\left(1 + \frac{E}{2mc^2 - V}\right)^{-1} \tag{51}$$

and expanding the term in parentheses is the basis of the so-called *regular approximations*, which were developed by the Amsterdam group [119,120] to a workable method for electronic-structure calculations.

A truncation of the expansion (51) defines the Zero- and First-Order Regular Approximation (ZORA,FORA) [121]. A particular noteworthy feature of ZORA is that even in the zeroth order there is an efficient relativistic correction for the region close to the nucleus, where the main relativistic effects come from. Excellent agreement of orbital energies and other valence shell properties with the results from the Dirac equation is obtained in this zero-order approximation, in particular in the Scaled ZORA variant [122], which takes the renormalization to the transformed large component approximately into account, using

$$\frac{1}{\sqrt{1 + X^\dagger X}} \approx \frac{1}{\sqrt{1 + \langle \phi_L X^\dagger | X \phi_L \rangle}} \tag{52}$$

The analysis [123] shows that in regions of high potential the zero-order Hamiltonian reproduces relativistic energies up to an error of order $-E^2/c^2$. On the other hand, in regions where the potential is small, but the kinetic energy of the particle high, the ZORA Hamiltonian does not provide any relativistic correction.

The main disadvantage of the method is its dependence on the zero point of the electrostatic potential, i. e., gauge dependence. This occurs because the potential enters non-linearly (in the denominator of the operator for the energy), so that a constant shift of the potential does not lead to a constant shift in the energy. This deficiency can, however, be approximately remedied by suitable means [122,124].

5.1.2 Transformation to two components

An alternative to the elimination-type methods is the attempt to achieve the block diagonalization of the Dirac operator according to (38) directly. The time-honoured method is the Foldy–Wouthuysen transformation [105]. The idea is to identify "odd" and "even" operators in the split form of the Dirac equation, i. e., operators which couple the large and small component, and such which do not. Apart from the even term $(\beta - 1)$, we can identify the even operator $\mathcal{E} = V$ and the odd operator $\mathcal{O} = c\boldsymbol{\alpha p}$, and find

$$[\mathcal{E}, \beta] = 0, \qquad \{\mathcal{O}, \beta\} = 0. \tag{53}$$

The braces denote the anticommutator $\{A, B\} = AB + BA$. We now look for a unitary matrix which removes the odd term. The Foldy–Wouthuysen transformation uses the ansatz

$$\begin{aligned} \Phi_1 &= \exp(iS_1)\Phi, \\ H_1 &= H + i\,[S_1, H] + \ldots \end{aligned} \tag{54}$$

The choice $S_1 = -i\beta\mathcal{O}/2m$ removes the odd term, but introduces new odd terms of higher order, which are in turn removed by iteration of the transformation :

$\Phi_n = \exp(iS_n)\Phi_{n-1}$. At this point, the resulting operators are again expanded in a power series in c^{-1}. Up to second order, we obtain again the Pauli Hamiltonian, Eq. (50). While different expressions occur in higher orders, the problems with singular operators are essentially the same as in the case of the Elimination of the Small Component discussed above. Additional problems occur, since the wave functions obtained in the Foldy–Wouthuysen procedure are no longer analytic functions of c^{-1} in the neighborhood of $c^{-1} = 0$ [125,126], as is the case for the Dirac wave function [127]. This means that the non-relativistic limit is not well defined.

To obtain a valid limiting procedure for $c^{-1} \to 0$, the perturbation theory has to be formulated by considering the non-relativistic limit of the metric (essentially the normalization requirement) and that of the operator itself separately. Both for the metric and for the operator limiting procedures must be defined. This is most conveniently done by formulating the Dirac equation in terms of a scaled small component $c\psi_S$, and a regular perturbation formalism results [128,127,129,130,131,125,126]. In the more recent literature, this four-component method has been dubbed Direct Perturbation Theory. The second-order results are equivalent to the perturbative results of the Pauli operator in an infinite basis set. In contrast to the singular expansions which are traditionally employed to derive the Pauli operator, Direct Perturbation Theory gives workable and regular results also for higher orders.

Another possibility which has meanwhile proven of considerable practical value is to avoid expansion in reciprocal powers of c throughout, and rather expand in the coupling strengh $Z\alpha c\hbar$, if closed expressions cannot be obtained [107,108,132].

The Douglas–Kroll (DK) transformation defines a transformation of the external-field Dirac Hamiltonian to two-component form which leads, in contrast to the Foldy–Wouthuysen transformation, to operators which are bounded from below and can be used variationally, similar to the Regular Approximations discussed above. As in the FW transformation, it is not possible in the DK formalism to give the transformation in closed form. It is rather defined by a sequence of unitary transformations $U_0, U_1, \ldots$, the first of which is in fact a free-particle Foldy–Wouthuysen transformation defined by

$$U_0 = A(1 + \beta R), \qquad U_0^{-1} = (R\beta + 1)A, \tag{55}$$

with

$$A = \sqrt{\frac{E_p + mc^2}{2E_p}} \tag{56}$$

$$R = \frac{c\boldsymbol{\alpha}\,\boldsymbol{p}}{E_p + mc^2} \tag{57}$$

$$E_p = c\sqrt{p^2 + m^2c^2}. \tag{58}$$

Applying U_0 to D leads to

$$U_0 D U_0^{-1} = \beta E_p + \mathcal{E}_1 + \mathcal{O}_1 \equiv H_1 \tag{59}$$

with even and odd operators of first order, given by

$$\begin{aligned} \mathcal{E}_1 &= A(V + RVR)A\ , \\ \mathcal{O}_1 &= \beta A(RV - VR)A\ . \end{aligned} \tag{60}$$

The following unitary transformation — it turns out that only one more is required to decouple the upper and lower components to sufficient accuracy for chemical applications — is defined by the somewhat unusual parametrization

$$U_1 = \sqrt{1 + W_1^2} + W_1. \tag{61}$$

For any anti-hermitean operator W_1 with $W_1^\dagger = -W_1$, it is easily seen that U_1 is unitary. Performing the transformation through U_1 and expanding the square root in powers of W_1 leads to

$$\begin{aligned} U_1 H_1 U_1^{-1} = \beta E_p - [\beta E_p, W_1] + \mathcal{E}_1 + \mathcal{O}_1 \\ + \frac{1}{2}\beta E_p W_1^2 + \frac{1}{2} W_1^2 \beta E_p - W_1 \beta E_p W_1 \\ + [W_1, \mathcal{O}_1] + [W_1, \mathcal{E}_1] + \ldots \end{aligned} \tag{62}$$

where the dots denote terms in higher than second order of W_1. The first-order odd term is now eliminated by equating

$$[\beta E_p, W_1] = \mathcal{O}_1 \tag{63}$$

and solving for W_1. We arrive at a momentum-space integral operator for W_1

$$W_1 \Phi(\boldsymbol{p}) = \int d^3p' \; W_1(\boldsymbol{p}, \boldsymbol{p'}) \Phi(\boldsymbol{p'}) \tag{64}$$

with a kernel

$$W_1(\boldsymbol{p}, \boldsymbol{p'}) = A(R - R') A' \frac{V(\boldsymbol{p}, \boldsymbol{p'})}{E_{p'} + E_p}, \tag{65}$$

where $V(\boldsymbol{p}, \boldsymbol{p'})$ denotes the Fourier transform of the external potential, and the primed quantities are to be expressed in terms of the variable $\boldsymbol{p'}$.

The final result is

$$H^{\text{decoupled}} \approx \beta E_p + \mathcal{E}_1 - \beta (W_1 E_p W_1 + \frac{1}{2}[{W_1}^2, E_p]), \tag{66}$$

where the approximation sign denotes equivalence up to second order in the external potential. Higher-order transformations may be devised by definitions similar to Eq. (61) in order to remove odd terms of higher order in a way similar to the method described above. The performance of the second-order operator was found satisfactory for chemical applications. At this point, a projection to the upper components may be made, with the result that the β matrix becomes the unit matrix, and the $\boldsymbol{\alpha}$ matrices are to be replaced by $\boldsymbol{\sigma}$ matrices.

The no-pair Hamiltonian $\hat{H}_+$ including all spin-dependent terms now operates on the two upper components only and is obtained as [133,134,5]

$$\hat{H}_+ = \sum_i E_p(i) + \sum_i V_{\text{eff}}(i) + \frac{1}{2} \sum_{i \neq j} V_{\text{eff}}(i,j) \; , \tag{67}$$

with

$$E_p(i) = \sqrt{p^2c^2 + m^2c^4},$$

$$V_{\rm eff}(i) = \sqrt{\frac{E_i + mc^2}{2E_i}}\,[V + (\boldsymbol{\sigma}_i\mathbf{P}_i)V(i)(\boldsymbol{\sigma}_i\mathbf{P}_i)]\,\sqrt{\frac{E_i + mc^2}{2E_i}},$$

$$\begin{aligned} V_{\rm eff}(i,j) = A_iA_j\Bigg[&\frac{1}{r_{ij}} + (\boldsymbol{\sigma}_i\mathbf{P}_i)\frac{1}{r_{ij}}(\boldsymbol{\sigma}_i\mathbf{P}_i) + (\boldsymbol{\sigma}_j\mathbf{P}_j)\frac{1}{r_{ij}}(\ \boldsymbol{\sigma}_j\mathbf{P}_j) \\ &+(\boldsymbol{\sigma}_i\mathbf{P}_i)(\boldsymbol{\sigma}_j\mathbf{P}_j)\frac{1}{r_{ij}}(\boldsymbol{\sigma}_i\mathbf{P}_i)(\boldsymbol{\sigma}_j\mathbf{P}_j) + \hat{B}_{ij}(\boldsymbol{\sigma}_i\mathbf{P}_i)(\boldsymbol{\sigma}_j\mathbf{P}_j) \\ &+(\boldsymbol{\sigma}_i\mathbf{P}_i)B_{ij}(\boldsymbol{\sigma}_j\mathbf{P}_j) + (\boldsymbol{\sigma}_j\mathbf{P}_j)B_{ij}(\boldsymbol{\sigma}_i\mathbf{P}_i) + (\boldsymbol{\sigma}_i\mathbf{P}_i)(\boldsymbol{\sigma}_j\mathbf{P}_j)B_{ij}\Bigg]A_iA_j, \end{aligned}$$

$$A_i = \sqrt{\frac{E_i + mc^2}{2E_i}},$$

$$\mathbf{P}_i = \frac{c\mathbf{p}_i}{E_i + mc^2},$$

$$\hat{B}_{ij} = -\frac{1}{2}\frac{1}{r_{ij}}\left[\boldsymbol{\sigma}_i\cdot\boldsymbol{\sigma}_j + (\ \boldsymbol{\sigma}_i\cdot\frac{\mathbf{r}_{ij}}{r_{ij}})(\boldsymbol{\sigma}_j\cdot\frac{\mathbf{r}_{ij}}{r_{ij}})\right].$$

Making repeated use of the Dirac relation

$$(\boldsymbol{\sigma}\mathbf{u})(\boldsymbol{\sigma}\mathbf{v}) = \mathbf{u}\mathbf{v} + i\boldsymbol{\sigma}(\mathbf{u}\times\mathbf{v}), \tag{68}$$

which is valid for operators $\mathbf{u}$ and $\mathbf{v}$ not containing $\boldsymbol{\sigma}$ matrices, terms linear in either one of the $\boldsymbol{\sigma}$ matrices are extracted. These terms constitute, per definition, the spin–orbit interaction part of the operator $\hat{H}_+$. There are, of course, spin-independent terms characteristic for relativistic kinematics, which constitute the above-mentioned "scalar relativistic" part of the operator, and terms with more than one $\boldsymbol{\sigma}$ matrix which contribute, e. g., to spin-spin coupling mechanisms. The spin–orbit part of the one-electron effective potential and the two-electron spin–orbit part resulting from the Coulomb interaction reduces to the spin–same–orbit interaction

$$\begin{aligned} \hat{H}_{\rm so}^{\rm same-orbit} = &\sum_i A_i i\boldsymbol{\sigma}_i(\mathbf{P}_iV(i)\times\mathbf{P}_i)A_i \\ &+\frac{1}{2}\sum_{i\neq j}A_iA_j\left[i\boldsymbol{\sigma}_i(\mathbf{P}_i\frac{1}{r_{ij}}\times\mathbf{P}_i) + i\boldsymbol{\sigma}_j(\mathbf{P}_j\frac{1}{r_{ij}}\times\mathbf{P}_j)\right]A_iA_j, \end{aligned} \tag{69}$$

and the extraction of the terms linear in $\boldsymbol{\sigma}_i$ and $\boldsymbol{\sigma}_j$ from the Breit contributions constitute the spin–other–orbit interaction [133]

$$\hat{H}_{\rm so}^{\rm other-orbit} = -\frac{1}{2}\sum_{i\neq j}A_iA_j\left[2i\boldsymbol{\sigma}_i(\mathbf{P}_i\frac{1}{r_{ij}}\times\mathbf{P}_j) + 2i\boldsymbol{\sigma}_j(\mathbf{P}_j\frac{1}{r_{ij}}\times\mathbf{P}_i)\right]A_iA_j. \tag{70}$$

Collecting terms, rearranging, and introducing explicitly the Coulomb potential of the nuclei, we obtain [5] a workable expression for a variationally stable spin–orbit operator

$$\hat{H}^{+}_{\rm so} = \sum_i \sum_\alpha c^2 Z_\alpha \, \frac{A_i}{E_i + mc^2} \, \boldsymbol{\sigma}_i (\frac{\mathbf{r}_{i\alpha}}{r^3_{i\alpha}} \times \mathbf{p}_i) \, \frac{A_i}{E_i + mc^2} \\ - c^2 \sum_{i \neq j} \frac{A_i A_j}{E_i + mc^2} \, (\frac{\mathbf{r}_{ij}}{r^3_{ij}} \times \mathbf{p}_i) \cdot (\boldsymbol{\sigma}_i + 2\boldsymbol{\sigma}_j) \, \frac{A_i A_j}{E_i + mc^2}. \tag{71}$$

In the case of singlet ground states well separated from the rest of the spectrum, it is often convenient to use the spin–averaged approximation and treat the spin–orbit coupling operator in a second step, be it perturbatively or variationally in a spin–orbit configuration interaction procedure with two-component spinors. In most applications (see, however, [134,135]) the DK transformation of the external potential V is limited to its one-electron part while the two-electron terms are left in their Coulomb form. This leads to the most frequently used spin-averaged 1–component many-electron no-pair Hamiltonian:

$$H_+ = \sum_i E_p(i) + \sum_i V_{\rm eff}(i) + \sum_{i<j} \frac{1}{r_{ij}}, \tag{72}$$

where

$$V_{\rm eff}(i) = -A_i [V(i) + \boldsymbol{P}_i V(i) \boldsymbol{P}_i] A_i \\ - W_1(i) E_p(i) W_1(i) - \frac{1}{2} [(W_1(i))^2, E_p(i)]. \tag{73}$$

Since the prefactors $(E_i + mc^2)^{-1}$ grow asymptotically (for $|p_i| \to \infty$, i. e., $r_i \to 0$) like $1/|\mathbf{p}_i|$, all contributions of momentum operators in the numerator (leading to the $1/r^3$ divergence in the case of the Breit–Pauli operator) are cancelled asymptotically, and only a Coulomb singularity remains. The Breit-Pauli operator may be recovered by reintroducing c explicitly, expanding $A_i(E_i + mc^2)^{-1}$ into powers of c^{-2}

$$\frac{A_i}{E_i + mc^2} = \frac{1}{2mc^2} - \frac{3p_i^2}{16m^3c^4} + \ldots \tag{74}$$

and keeping only the lowest-order term.

Douglas–Kroll-transformed Hamiltonians have been used in many quantum-chemical calculations on molecules, density-functional theory [136] including implementation of derivatives [137], and recently also for calculations of solids [138,139,140]. A numerical analysis of the energy values [108,141] and also perturbation theory [103] shows that the eigenvalues of the second-order Douglas–Kroll-transformed Hamiltonian for a single particle agrees with the results of the Dirac equation to order c^{-4}. Note that this is the same order in which deviations in the matrix representation of the Dirac equation itself are expected [142,103].

The Douglas–Kroll transformation can be carried to higher orders, if desired [143]. In this way, arbitrary accuracy with respect to the eigenvalues of D can be achieved, and many applications of this method are reported in the literature [144,145,146,147].

The most elaborate of these methods based on the Douglas–Kroll transformation is again of the coupled-cluster type and has been published recently [148]. It possesses many of the essential features of the 4-component approach, including the description of spin–orbital and spin–spin interactions. The CdH molecule and its ions were chosen for the pilot application of two- and four-component Fock-Space RCC [148]. The calculated values were obtained in very good agreement with experiment. While the four-component method gives the best results, one- and two-component calculations include almost all the relativistic effects. Since they are much cheaper than four-component calculations, they offer a viable alternative for systems with heavy atoms.

6 Epilogue

In this account, we presented some of the recent devolpments in relativistic electronic structure theory for atoms and molecules. The field has seen a tremendous development during the last two decades. Especially approximate relativistic operators have been studied during this period. It took quite a long time until it was realized that a meaningful description of the structure of atoms and molecules containing heavy atoms can only be achieved on a relativistic basis.

References

1. K. S. Pitzer. *Acc. Chem. Res.*, 12(8):271–276, August 1979.
2. P. Pyykkö and J.-P. Desclaux. *Acc. Chem. Res.*, 12(8):276–281, August 1979.
3. P. Pyykkö. *Chem. Rev.*, 88:563–594, 1988.
4. W. H. E. Schwarz, A. Rutkowski, and S. G. Wang. *Int. J. Quantum Chem.*, 57:641–653, 1996.
5. B. A. Heß. *Ber. Bunsenges. Phys. Chem.*, 101:1, 1997.
6. P. Pyykkö. *Relativistic Theory of Atoms and Molecules - A Bibliography 1916-1985*, volume 41 of *Lecture Notes in Chemistry*. Springer-Verlag, Berlin, 1986.
7. P. Pyykkö. *Relativistic Theory of Atoms and Molecules II - A Bibliography 1986-1992*, volume 60 of *Lecture Notes in Chemistry*. Springer-Verlag, Berlin, 1993.
8. P. Pyykkö. Database 'RTAM' (relativistic quantum chemistry database 1915-1998; http://www.csc.fi/lul/rtam/rtamquery.html), 1999.
9. A. Hibbert. *Rep. Prog. Phys.*, 38:1217–1338, 1975.
10. W. R. Johnson and K. T. Cheng. *(in: Atomic Inner-Shell Physics)*, pages 3–30. Physics of Atoms and Molecules. Plenum Press, New York, London, 1985.
11. I. P. Grant. *Adv. At. Mol. Opt. Phys.*, 32:169–186, 1994.
12. B. Swirles. *Proc. Roy. Soc. London A*, 152:625–649, 1935.
13. B. R. Judd. *Operator Techniques in Atomic Spectroscopy*. Princeton Landmarks in Physics. Princeton University Press, Princeton NJ, 1998.
14. A. R. Edmonds. *Angular Momentum in Quantum Mechanics*. Princeton Landmarks in Physics. Princeton University Press, Princeton NJ, 1996.
15. I. P. Grant. *Proc. Roy. Soc. London A*, 262:555–576, 1961.

16. I. P. Grant. *Proc. Phys. Soc.*, 86:523–527, 1965.
17. I. P. Grant. *Adv. Phys.*, 19:747–811, 1970.
18. Y.-K. Kim. *Phys. Rev.*, 154(1):17–39, February 1967.
19. J. P. Desclaux. *At. Data Nucl. Data Tables*, 12(4):311–406, 1973.
20. J. P. Desclaux. *Comp. Phys. Comm.*, 9:31–45, 1975.
21. I. P. Grant, B. J. McKenzie, P. H. Norrington, D. F. Mayers, and N. C. Pyper. *Comp. Phys. Comm.*, 21:207–231, 1980.
22. B. J. McKenzie, I. P. Grant, and P. H. Norrington. *Comp. Phys. Comm.*, 21:233–246, 1980.
23. K. G. Dyall, I. P. Grant, C. T. Johnson, F. A. Parpia, and E. P. Plummer. *Comp. Phys. Comm.*, 55:425–456, 1989.
24. K. G. Dyall. *GRASP - Users' Manual*. Oxford, March 1988.
25. J. P. Desclaux, D. F. Mayers, and F. O'Brien. *J. Phys. B: Atom. Molec. Phys.*, 4:631–642, 1971.
26. F. A. Parpia, C. F. Fischer, and I. P. Grant. *Comp. Phys. Comm.*, 94:249, 1996.
27. H. M. Quiney, I. P. Grant, and S. Wilson. *J. Phys. B: At. Mol. Phys.*, 20:1413–1422, 1987.
28. H. M. Quiney, I. P. Grant, and S. Wilson. *J. Phys. B: At. Mol. Opt. Phys.*, 23:L271–L278, 1990.
29. F. A. Parpia and A. K. Mohanty. *Phys. Rev. A*, 46(7):3735–3745, October 1992.
30. K. G. Dyall, P. R. Taylor, K. Faegri. Jr., and H. Partridge. *J. Chem. Phys.*, 95(4):2583–2594, August 1991.
31. O. Visser, L. Visscher, P. J. Aerts, and W. C. Nieuwpoort. *Theor. Chim. Acta*, 81:405–416, 1992.
32. K. G. Dyall. *(in: Relativistic and Electron Correlation Effects in Molecules and Solids)*, volume 318 of *NATO ASI Series; Series B: Physics*, pages 17–58. Plenum Press, New York, 1994.
33. W. C. Nieuwpoort, P. J. C. Aerts, and L. Visscher. *(in: Relativistic and Electron Correlation Effects in Molecules and Solids)*, volume 318 of *NATO ASI Series; Series B: Physics*, pages 59–70. Plenum Press, New York, 1994.
34. H. J. Aa. Jensen, K. G. Dyall, T. Saue, and . Jr. K. Fægri. *J. Chem. Phys.*, 104(11):4083–4097, March 1996.
35. T. Saue, K. Fægri, T. Helgaker, and O. Gropen. *Mol. Phys.*, 91:937–950, 1997.
36. L. Szasz. *The Electronic Structure of Atoms*. John Wiley & Sons, New York, 1992.
37. L. F. Richardson. *Phil. Trans. Roy. Soc. London A*, 210:307–357, 1910.
38. C.-E. Fröberg. *Numerical Mathematics - Theory and Computer Applications*. The Benjamin/Cummings Publishing Company, Menlo Park, 1. edition, 1985.
39. W. G. Bickley. *Mathematical Gazette*, 25:19–27, 1941.
40. M. Abramowitz and I. A. Stegun. *Handbook of Mathematical Functions*. Dover Publications, New York, 9. edition, 1972.
41. C. Froese. Fischer. *The Hartree-Fock Method for Atoms*. John Wiley & Sons, New York, 1. edition, 1977.

42. C. Froese. Fischer, T. Brage, and P. Jönsson. *Computational Atomic Structure — An MCHF Approach*. Institute of Physics Publishing, Bristol, Philadelphia, 1997.
43. D. Andrae and J. Hinze. *Int. J. Quantum Chem.*, 63:65–91, 1997.
44. D. Andrae, M. Reiher, and J. Hinze. *Int. J. Quantum Chem.*, in press 2000.
45. J. P. Desclaux. *(in: Methods and Techniques in Computational Chemistry: METECC-94)*, volume A – Small Systems, pages 253–274. STEF, Cagliari, 1993.
46. F. Biegler-König. Fakultät für Chemie, Universität Bielefeld, unpublished.
47. W. H. Press, S. A. Teukolsky, W. T. Vetterling, and B. P. Flannery. *Numerical Recipes in Fortran — The Art of Scientific Computing*. Cambridge University Press, Cambridge, 2. edition, 1992.
48. C. Brezinski and M. Redivo. Zaglia. *Extrapolation Methods — Theory and Practice*, volume 2 of *Studies in Computational Mathematics*. North-Holland, 1991.
49. P. Deuflhard and A. Hohmann. *Numerische Mathematik — Eine algorithmisch orientierte Einführung*. Walter de Gruyter, Berlin, 1991.
50. G. Breit. *Phys. Rev.*, 34 (2. Ser.)(4):553–573, August 1929.
51. G. Breit. *Phys. Rev.*, 36(3):383–397, August 1930.
52. G. Breit. *Phys. Rev.*, 39:616–624, February 1932.
53. I. P. Grant and N. C. Pyper. *J. Phys. B: Atom. Molec. Phys.*, 9(5):761–774, 1976.
54. M. Reiher and J. Hinze. *J. Phys. B*, 32:5489–5505, December 1999.
55. M. Reiher. PhD thesis, Fakultät für Chemie, Universität Bielefeld, 1998.
56. P. J. Mohr, G. Plunien, and G. Soff. *Phys. Rep.*, 293:227–369, 1998.
57. E. R. Davidson. *J. Comp. Phys.*, 17:87–94, 1975.
58. C. W. Murray, S. C. Racine, and E. R. Davidson. *J. Comp. Phys.*, 103:382–389, 1992.
59. J. Bieroń, P. Jönsson, and C. Froese. Fischer. *Phys. Rev. A*, 53(4):2181–2188, April 1996.
60. P. Pulay. *Chem. Phys. Lett.*, 73(2):393–398, July 19.
61. P. Pulay. *J. Comp. Chem.*, 3:556–560, 1982.
62. T. H. Fischer and J. Almlöf. *J. Phys. Chem.*, 96:9768–9774, 1992.
63. H. J. J. van Dam, J. H. van Lenthe, G. L. G. Sleijpen, and H. A. van der Vorst. *Int. J. Quantum Chem.*, 17:267, 1996.
64. H. A. van der Vorst and G. L. G. Sleijpen. volume 1184 of *Lect. Notes Comp. ScienceApplie*, pages 686–696. Springer-Verlag, Berlin, 1996.
65. H. A. Van der Vorst and T. F. Chan. *Linear System Solvers: Sparse Iterative Methods (in: Parallel Numerical Algorithms)*, volume 4 of *ICASE/LaRC Interdisc. Ser. in Science and Engineering*, pages 167–202. Kluwer Academic, Dordrecht, 1997.
66. G. H. Golub and H. A. van der Vorst. *Closer to the solution: Iterative linear solvers (in: The State of the Art in Numerical Analysis)*, pages 63–92. Clarendon Press, Oxford, 1997.
67. H. A. van der Vorst and G. H. Golub. *150 Years old and still alive: eigenproblems (in: The State of the Art in Numerical Analysis)*, pages 93–119.

Clarendon Press, Oxford, 1997.
68. J. Sucher. *Phys. Rev. A*, 22:348–362, 1980.
69. W. Buchmüller and K. Dietz. *Z. Phys. C*, 5:45, 1980.
70. I. Lindgren. *Many-Body Methods in Quantum Chemistry, edited by U. Kaldor*, page 293. Springer-Verlag, 1989.
71. R. J. Bartlett. *Modern Electronic Structure Theory, edited by D. R. Yarkony*, page 1047. World Scientific, Singapore, 1995.
72. E. Lindroth. *Phys. Rev. A*, 37:316, 1988.
73. A.-M. Mårtensson-Pendrill. *Numerical Determination of the Electronic Structure of Atoms, Diatomic and Polyatomic Molecule, edited by M. Defranceschi and J. Delhalle*, page 131. Kluwer, 1989.
74. S. A. Blundell, W. R. Johnson, Z. W. Liu, and J. Sapirstein. *Phys. Rev. A*, 39:3768, 1989.
75. S. A. Blundell, W. R. Johnson, Z. Liu, and J. Sapirstein. *Phys. Rev. A*, 40:2233, 1989.
76. Z. W. Liu and H. P. Kelly. *Phys. Rev. A*, 43:3305, 1991.
77. S. A. Blundell, W. R. Johnson, and J. Sapirstein. *Phys. Rev. Lett.*, 65:1411, 1990.
78. S. A. Blundell, W. R. Johnson, and J. Sapirstein. *Phys. Rev. A*, 43:3407, 1991.
79. H. Sekino and R. J. Bartlett. *Int. J. Quantum Chem.*, 24:241, 1990.
80. A.-M. Mårtensson-Pendrill, S. A. Alexander, L. Adamowicz, N. Oliphant, J. Olsen, P. Öster, H. M. Quiney, S. Salomonson, and D. Sundholm. *Phys. Rev. A*, 43:3355, 1991.
81. E. Ilyabaev and U. Kaldor. *Chem. Phys. Lett.*, 194:95, 1992.
82. E. Ilyabaev and U. Kaldor. *Phys. Rev. A*, 47:137, 1993.
83. E. Ilyabaev and U. Kaldor. *J. Chem. Phys.*, 98:7126, 1992.
84. E. Eliav, U. Kaldor, and Y. Ishikawa. *Chem. Phys. Lett.*, 222:82, 1994.
85. E. Eliav, U. Kaldor, and Y. Ishikawa. *Phys. Rev. A*, 50:1121, 1994.
86. E. Eliav, U. Kaldor, and Y. Ishikawa. *Phys. Rev. A*, 49:1724, 1994.
87. E. Eliav, U. Kaldor, and Y. Ishikawa. *Int. J. Quantum Chem. Symp.*, 28:205, 1994.
88. E. Eliav, U. Kaldor, P. Schwerdtfeger, B. A. Heß, and Y. Ishikawa. *Phys. Rev. Lett.*, 73:3203–3206, 1994.
89. E. Eliav, U. Kaldor, and Y. Ishikawa. *Phys. Rev. Lett.*, 74:1079, 1995.
90. E. Eliav, U. Kaldor, and Y. Ishikawa. *Phys. Rev.*, 51:225, 1995.
91. E. Eliav, U. Kaldor, and Y. Ishikawa. *Phys. Rev. Lett.*, 77:5350, 1996.
92. E. Eliav, U. Kaldor, Y. Ishikawa, M. Seth, and P. Pyykkö. *Phys. Rev. A*, 53:3926–3933, 1996.
93. L. Visscher, T. Saue, W. C. Nieuwpoort, K. Fægri, and O. Gropen. *J. Chem. Phys.*, 99:6704–6715, 1993.
94. K. G. Dyall. *Chem. Phys. Lett.*, 224:186–194, 1994.
95. L. Visscher, K. G. Dyall, and T. J. Lee. *Int. J. Quantum Chem. Symp.*, 29:411, 1995.
96. L. Visscher, K. G. Dyall, and T. J. Lee. *J. Chem. Phys.*, 105:8769, 1996.
97. L. Visscher and K. G. Dyall. *J. Chem. Phys.*, 104:9040, 1996.

98. E. Eliav and U. Kaldor. *Chem. Phys. Lett.*, 248:405, 1996.
99. J. J .Å. Jensen, K. G. Dyall, T. Saue, and K. Fægri. Jr. *J. Chem. Phys.*, 104:4083–4097, 1996.
100. K. G. Dyall. *J. Chem. Phys.*, 100:2118–2127, 1994.
101. Ch. Chang, M. Pélissier, and Ph. Durand. *Phys. Scr.*, 34:394–404, 1986.
102. J. L. Heully, I. Lindgren, E. Lindroth, S. Lundquist, and A. M. Mårtensson-Pendrill. *J. Phys. B*, 19:2799–2815, 1986.
103. W. Kutzelnigg. *Chem. Phys.*, 224:203–222, 1997.
104. A. G. Nikitin. *J. Phys. A*, 31:3297–3300, 1998.
105. L. L. Foldy and S. A. Wouthuysen. *Phys. Rev.*, 78:29–36, 1950.
106. J. D. Morrison and R. E. Moss. *Mol. Phys.*, 41:491–507, 1980.
107. M. Douglas and N. M. Kroll. *Ann. Phys. (N.Y.)*, 82:89–155, 1974.
108. B. A. Heß. *Phys. Rev. A*, 33:3742–3748, 1986.
109. P. O. Löwdin. *J. Molec. Spectr.*, 14:131–144, 1964.
110. R. D. Cowan and D. C. Griffin. *J. Opt. Soc. Am.*, 66:1010–1014, 1976.
111. J. H. Wood and A. M. Boring. *Phys. Rev. B*, 18:2701–2711, 1978.
112. J. C. Barthelat, M. Pélissier, and Ph. Durand. *Phys. Rev. A*, 21:1773–1785, 1980.
113. J. Karwowski and J. Kobus. *Chem. Phys.*, 55:361–369, 1981.
114. J. Karwowski and M. Szulkin. *J. Phys. B*, 15:1915–1925, 1982.
115. J. Karwowski and J. Kobus. *Int. J. Quantum Chem.*, 28:741–756, 1985.
116. J. Wood, I. P. Grant, and S. J. Wilson. *J. Phys. B*, 18:3027–3041, 1985.
117. K. G. Dyall. *J .Chem. Phys.*, 106:9618–9626, 1997.
118. K. G. Dyall. *J .Chem. Phys.*, 109:4201–4208, 1998.
119. E. van Lenthe, R. van Leeuwen, E. J. Baerends, and J. G. Snijders. *New Challenges in Computational Quantum Chemistry, edited by R. Broer, P. J. C. Aerts and P. S. Bagus*, pages 93–111. 1995.
120. E. van Lenthe, R. van Leeuwen, E. J. Baerends, and J. G. Snijders. *Int. J. Quantum Chem.*, 57:281–293, 1996.
121. E. van Lenthe, E. J. Baerends, and J. G. Snijders. *J. Chem. Phys.*, 99:4597–4610, 1993.
122. E. van Lenthe, E. J. Baerends, and J. G. Snijders. *J. Chem. Phys.*, 101:9783–9792, 1994.
123. R. van Leeuwen, E. van Lenthe, E. J. Baerends, and J. G. Snijders. *J. Chem. Phys.*, 101:1271–1281, 1994.
124. C. van Wüllen. *J. Chem. Phys*, 109:392–400, 1998.
125. W. Kutzelnigg. *Z. Phys. D*, 11:15–28, 1989.
126. W. Kutzelnigg. *Z. Phys. D*, 15:27–50, 1989.
127. E. C. Titchmarsh. *Proc. Roy. Soc. (London)*, A266:33–46, 1962.
128. G. L. Sewell. *Proc. Camb. Phil. Soc.*, 45:631–637, 1949.
129. A. Rutkowski. *J. Phys. B*, 19:149–158, 1986.
130. A. Rutkowski. *J. Phys. B*, 19:3431–3442, 1986.
131. A. Rutkowski. *J. Phys. B*, 19:3443–3455, 1986.
132. G. Jansen and B. A. Heß. *Phys. Rev. A*, 39:6016–6017, 1989.
133. R. Samzow and B. A. Heß. *Chem. Phys. Lett.*, 184:491–495, 1991.
134. R. Samzow, B. A. Heß, and G. Jansen. *J. Chem. Phys.*, 96:1227–1231, 1992.

135. C-Y. Park and J. E. Almlöf. *Chem. Phys. Lett.*, 231:269–276, 1994.
136. O. D. Häberlen and N. Rösch. *Chem. Phys. Lett.*, 199:491–496, 1992.
137. V. A. Nasluzov and N. Rösch. *Chem. Phys.*, 210:413–425, 1996.
138. N. J. M. Geipel and B. A. Heß. *Chem. Phys. Lett.*, 273:62–70, 1997.
139. J. C. Boettger. *Phys. Rev. B*, 57:8743–8746, 1998.
140. G. M. Fehrenbach and G. Schmidt. *Phys. Rev. B*, 55:6666–6669, 1997.
141. K. Molzberger and W. H. E. Schwarz. *Theor. Chim. Acta*, 94:213–222, 1996.
142. R. E. Stanton and S. Havriliak. *J. Chem. Phys.*, 81:1910–1918, 1984.
143. M. Barysz, A. J. Sadlej, and J. G. Snijders. *Int. J. Quantum Chem.*, 65:225–239, 1997.
144. U. Kaldor and B. A. Heß. *Chem. Phys. Lett.*, 230:1–7, 1994.
145. M. Seth, P. Schwerdtfeger, M. Dolg, K. Fægri, B. A. Heß, and U. Kaldor. *Chem. Phys. Lett*, 250:461–465, 1996.
146. C. L. Collins, K. D. Dyall, and H. F. Schaefer. III. *J. Chem. Phys.*, 102:2024, 1995.
147. V. Kellö, A. J. Sadlej, and B. A. Heß. *J. Chem. Phys.*, 105:1995–2003, 1996.
148. E. Eliav, U. Kaldor, and B. A. Heß. *J. Chem. Phys.*, 108:3409–3415, 1998.